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TEMPERATURE RESPONSIVE MEMBRANE FILTER
[Ondo outousei rokamaku]

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TITLE (54) : TEMPERATURE RESPONSIVE MEMBRANE FILTER

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1. Title of the Invention

Temperature responsive membrane filter

2. Claims

1. A temperature responsive membrane filter, characterized by the facts that a macromolecular chain is implanted on the surface layer and pore portion of a porous membrane filter, a pronounced conformation change at the lower critical solution temperature (hereunder called LCST) of said macromolecular chain is utilized, thus causing the pore diameter to be changed, and the membrane permeation properties are adjusted within a narrow temperature range in the vicinity of said temperature.

2. A temperature responsive membrane filter according to Claim 1, characterized by the fact that the macromolecular chain is implanted by a surface graft copolymerization technique on the surface layer and pore portion of the porous membrane filter.

3. A temperature responsive membrane filter according to Claim 1 or Claim 2, characterized by the fact that a polyisopropyl acrylamide macromolecular chain is implanted on a porous membrane filter of polyvinylidene fluoride of superior dimensional stability and dynamic strength.

4. A temperature responsive membrane filter according to any of Claims 1 through 3, characterized by the fact that the response

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temperature is optionally adjusted by the selection of a copolymer having a [specific] composition ratio of a polyisopropyl acrylamide and another hydrophilic or hydrophobic macromolecule, for the macromolecular chain that is implanted on the surface layer and pore portion of the porous membrane filter.

3. Detailed Explanation of the Invention

The present invention pertains to a macromolecular membrane proposed so as to make it possible to adjust the filtration properties in response to temperature. Recently much research has been advancing in relation to the development of a macromolecular film that changes its filtration properties and macromolecular material such as gel that changes shape, for example, in response to external stimulus. If these materials can be made practical, application to a wide variety of fields is anticipated, such as to medical materials and flow engineering, for example. The mode of external stimulation can be classified into at least 2 types: 1) impartation of energy, and 2) addition of material. The energy of type 1) can conceivably be realized as: (1) dynamic energy such as pressure or shock; (2) application of electrical energy; (3) application of an electrical field or magnetic field; (4) irradiation of light; (5) application of thermal energy; and (6) impartation of ultrasound, for example. The addition of material of type 2)

includes such things as the addition of a specific reagent that /2
directly contributes to a chemical reaction, or an operation called a
removal operation, as well as stimulation by changing the
concentration of various ions, beginning with a change of the
concentration of hydrogen ions (pH), and external stimulation by
changing the concentration of moisture that includes ambient
humidity.

Even though a gel, membrane, or valve, for example, is developed
that responds to external stimulus, in a case where the control
thereof must be operated remotely, some sort of pipe is required in
order to transmit the external stimulus. Nevertheless, this is not
necessary in a case where the object can be achieved merely by
responding to a range of external stimulus coming into direct contact
with the artificial organ, such as in an artificial organ, for
example, used within a human body, for example, which is subject to
changes in pH, changes in temperature, changes in insulin
concentration, and changes in glucose concentration, for example. It
is also unnecessary to transmit an external stimulus artificially in
a case where the objective to be controlled is automatically achieved
by the gel, valve, membrane, or other macromolecular material
responding to external air temperature, humidity, luminous energy, or
concentration of contaminating substances, for example. A
macromolecular material that responds automatically to external
stimulus as described in this way involves the development of a novel

material that has a completely different concept from the concept of depending entirely on an electrical signal for control, as would be the case for conventional water flow regulation from a remote location, for example.

Of the different kinds of external stimulus, the inventors directed their attention to temperature changes, and conducted diligent investigations in order to develop a macromolecular membrane for which membrane permeability could be controlled in response to ambient temperature change; as a result, they arrived at the present invention.

According to the present invention, a suitable macromolecular chain is implanted on the pore portion and surface layer of a porous membrane filter. Generally, a macromolecular chain takes a different conformation according to the temperature and the type of solvent that surrounds it. In a case where an ionic functional group is present on the macromolecular chain, such as a macromolecular electrolyte, a conformation is taken that differs according to changes in the various ion concentrations, with the list of examples beginning with the hydrogen ion concentration. The utilization of this phenomenon makes it possible to develop a macromolecular material responsive to external stimulus, but in a case where it has been assessed that what is needed is that the change triggered by the response is of a pronounced or rapid-response type, it has not hitherto been possible to make a material that satisfies these

assessed requirements. The inventors have paid attention to the fact that phase changes occur based upon pronounced and rapid-response-type conformation changes, arising from lower critical solution temperature (LCST) in the vicinity of ordinary temperature, such as polyisopropyl acrylamide for example. As shown in Figure 1, a macromolecular chain implanted in a pore portion and surface layer of a porous membrane filter is such that, at a temperature equal to or greater than the LCST, the effective pore diameter becomes larger and the amount of membrane-transiting substance increases greatly. Conversely, at a temperature equal to or less than the LCST, the implanted macromolecular chain closes the pore, and the permeability rate decreases.

There are no particular limitations on a substrate for a material used in a porous membrane filter, and it is conceivable to use a macromolecular material such as cellulose, polyvinyl acetate, nylon, polypropylene, and polysulfone, for example; however, since it is necessary to successfully implant a macromolecular chain easily by a technique such as by coating or by surface graft polymerization, a material such as polyvinylidene fluoride, which is widely utilized due to its superior dimensional stability and dynamic strength, is suitable. Mere swabbing or coating is acceptable as a method for implanting a macromolecular chain on the pore portion and surface phase of a porous membrane filter, but it is preferable to rely on chemical bonds due to a coupling reaction or surface graft

polymerization in order to increase the stability of bonding with the surface portion.

There are no limitations in particular on the type of macromolecular chain that is implanted on the surface portion; an ordinary macromolecule has a small conformation change due to temperature, so the use of a polymer such as an N-substituted acrylamide or methyl vinyl ether is conceivable; nevertheless, it is practical to use a polymer that has an LCST in the vicinity of ordinary temperature, such as polyisopropyl acrylamide, which makes it possible to control membrane permeability by small temperature changes. In order to adjust the control temperature region, a block copolymer is used, wherein a suitable composition ratio is selected for a hydrophobic or hydrophilic macromolecule such as butyl methacrylate, acrylamide, and the like, and for a macromolecule such as polyisopropyl acrylamide.

The advantages of the invented membrane filter are listed below.

1. It can be manufactured simply and inexpensively, merely by improving the surface portion of an existing membrane, without making a membrane that uses special materials.
2. Because it is possible to select a stable macromolecular material, and because it is possible to utilize a technique in which a macromolecular chain implanted on the surface portion is subjected to stable covalent bonding or surface graft polymerization, there is

almost no worry whatsoever of toxicity even if it is used in applications for medical devices that are implanted within a human body.

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3. A macromolecular chain conformation change due to temperature change is utilized, therefore the response time is rapid, and [the change] is reversible.

4. It is possible to set the response temperature region optionally by selecting the type of macromolecular chain and by selecting a copolymer having various composition ratios.

The present invention is explained below with reference to working examples.

Working Example 1

A porous polyvinylidene fluoride membrane having a pore diameter of 0.22 microns was subjected to a low-temperature argon plasma treatment for 10 minutes, then surface graft polymerization was conducted with isopropyl acrylamide using a photopolymerization technique at 10°C. The obtained surface grafted membrane showed a water passage rate 20 times greater at 35°C than at 30°C, and a high level that was 34 times greater at 40°C than at 30°C. For reference, note that the LCST of a 10% by weight aqueous solution of polyisopropyl acrylamide is 30 to 33°C.

Working Example 2

Graft polymerization was conducted by the same technique used in Working Example 1, with the exception that a monomer aqueous solution

of polyisopropyl acrylamide and acrylamide was used in 4-to-1 mole ratio. The obtained grafted film had a water passage rate 4 times greater at 60°C than at 52°C, and 18 times greater at 70°C than at 52°C. For reference, it has been demonstrated that the LCST of a 10% aqueous solution of copolymer obtained by a copolymerization reaction of polyisopropyl acrylamide and acrylamide in 4-to-1 mole ratio is 53 to 55°C.

Working Example 3

Graft polymerization was conducted by the same technique used in Working Example 1, with the exception that a monomer aqueous solution of polyisopropyl acrylamide and acrylamide was used in 7-to-3 mole ratio. The obtained grafted film had a water passage rate 6 times greater at 50°C than at 42°C, and 19 times greater at 60°C than at 42°C. For reference, it has been demonstrated that the LCST of a 10% by weight aqueous solution of copolymer obtained by a copolymerization reaction of polyisopropyl acrylamide and acrylamide in 7-to-3 mole ratio is 45 to 47°C.

Working Example 4

Graft polymerization was conducted by the same technique used in Working Example 1, [with the exception that] a monomer aqueous solution of polyisopropyl acrylamide and normal butyl acrylate was used in 49-to-1 mole ratio. The obtained grafted film had a water passage rate 9 times greater at 30°C than at 20°C, and 23 times greater at 35°C than at 24°C. For reference, it has been demonstrated

that the LCST of a 10% by weight aqueous solution of copolymer obtained by a copolymerization reaction of polyisopropyl acrylamide and normal butyl acrylate in 49-to-1 mole ratio is 24 to 26°C.

Working Example 5

The water permeation rate of the grafted membrane obtained in Working Example 1 was measured for a total of 10 cycles of alternation between water of 30°C and water of 40°C replaced at short intervals of 5 seconds or less, with the passage rate at the respective temperatures being measured for each interval. It was demonstrated that the rate for 40°C was 34 times greater than the rate at 30°C, at each measurement point. These findings demonstrate that the invented permeable membrane reversibly responds to temperature changes, and that the response time is satisfactorily rapid.

4. Brief Explanation of the Drawings

A schematic drawing of a permeable membrane according to the present invention is shown in Figure 1, where 1 indicates a cross-section of a porous membrane substrate, and 2 indicates a macromolecular chain. A pore at a temperature equal to or less than the LCST is represented by 3, and a pore at a temperature equal to or greater than the LCST is represented by 4.

Figure 1

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